



PtCu substrates subjected to AC and DC electric fields in a solution of benzene sulfonic acid–phenol as novel batteries and their use in glucose biofuel cells



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HIGHLIGHTS

- PtCu subjected to AC and DC fields in BSA-P or ABTS-P solutions generates power.
- FC based PtCu(BSA-PP-Pt-Cu) electrodes as anode and cathode reaches $10.8 \mu\text{W mm}^{-2}$.
- These kinds of electrodes can boost the power outputs of BFCs.
- Addition of enzymes GOx at the anode and LAC at the cathode yields $13.3 \mu\text{W mm}^{-2}$.

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ABSTRACT

We describe how bi-metal PtCu connected wires, immersed in a solution of benzene sulfonic acid (BSA)–phenol (P) or 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS)–phenol (P), then subjected to simultaneous alternating current (AC) and direct current (DC) electric fields generate power. We discovered that PtCu substrate covered by the deposit containing (BSA-PP-Pt-Cu), abbreviated as PtCu(BSA-PP-Pt-Cu) electrode, plays the role of a substantial anode and cathode. The latter was related to the formation of micro-batteries in the deposited film (BSA-PP-Pt-Cu) that are able to take or deliver electrons from the deposited Pt and Cu, respectively. PP-BSA plays probably the role of bridge for proton conduction in the formed micro-batteries. The power density of the fuel cell (FC)-based PtCu(BSA-PP-Pt-Cu) anode and PtCu(BSA-PP-Pt-Cu) cathode in phosphate buffer solution pH 7.4 at room temperature reaches $\sim 10.8 \mu\text{W mm}^{-2}$. Addition of enzymes, glucose oxidase at the anode and laccase at the cathode and, replacement of BSA by ABTS at the cathode in the deposited films increases the power density to $13.3 \mu\text{W mm}^{-2}$. This new procedure might be of great relevance for construction of a new generation of FCs operating at mild conditions or boost the power outputs of BFCs and make them suitable for diverse applications.

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1. Introduction

Today, energy market demands reliable, low cost and environmentally friendly energy sources. The development of more efficient energy conversion systems is one of the most important technological challenges for the twenty first century [1,2]. It is expected that fuel cells (FCs) systems play a key role. Accordingly, considerable efforts have been devoted to FCs development by

focusing on the performance, fabrication costs and, reduction in size/weight for use in portable devices [3–6].

There are various kinds of FCs such as polymer electrolyte membrane FCs, phosphoric acid FCs, alkaline FCs, solid oxide FCs and direct alcohol FCs [7]. Other categories of FCs such as biofuel cells (BFCs) based enzymes have also been intensively investigated [8–12]. The reason for that has to do with the environmental load that this technology offers. Compared to FCs, which operate under acidic or alkaline electrolyte solutions and high temperatures, BFCs employ neutral pH and ambient working temperatures. These conditions offer the possibility to be used for *in vivo* implantation in animals or humans as power sources for microelectronic devices such as sensors transmitters or artificial organs [13,14]. On the other hand, contrary to conventional FCs, BFCs such as glucose

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(GBFCs) suffer from severe limitations including low power and instability over time. Furthermore, most of the GBFCs are reported at substrate saturating conditions of glucose and O_2 [15]. Nevertheless, for *in vivo* implantation, the concentration of glucose and specially O_2 in the physiological fluids are remarkably lower than those corresponding to the saturating glucose conditions or dioxygen solubility in buffer. The latter constitute a key factor limiting the power of GBFCs. Recently, implantation of GBFC based graphite electrodes in rats has been reported [16]. However, these electrodes delivered only $0.05 \mu W \text{ mm}^{-2}$, a value far from that is required to supply implantable electronic devices. Therefore, the design of more powerful GBFCs is one of the major challenges for supplying implantable biomedical devices. To achieve high power GBFCs, some studies employed materials like carbon nanotubes (CNTs) and porous carbon [12,17–24]. Another alternative way to boost the power of BFCs is to take advantage of the materials that are used for FCs and employ them to BFCs under their operating conditions of neutral pH and ambient temperature.

In the last decades, there have been rising interests in the application of PtCu bi-metal nano-materials in FCs cathodes and anodes [25–32]. Furthermore, recent studies showed that PtCu bi-metal can be employed as nano-batteries autonomous nano-motors [33]. In the course of this study, we introduce a new type of electrode material based PtCu substrates that can generate sufficient power in the physiological electrolyte. Such electrodes might be of great relevance to be used as new electrodes platforms for a new generation of FCs that operate under neutral pH and ambient temperature or help to boost the power outputs of BFCs and make them suitable to supply implantable biomedical devices with sufficient energy.

2. Experimental

2.1. Materials

Ultrapure water milliQ grade with a resistivity of $18.2 \text{ M}\Omega \text{ cm}$ was used for all the experiments. Glucose oxidase (GOx) crude from *Aspergillus niger* (211 units/mg) and laccase (Lac) from *Trametes versicolor* (24 units/mg) were purchased from Sigma. Pyrrole (Py), phenol (P), benzene sulfonic acid (BSA) and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) from Sigma–Aldrich. Platinum (Pt) and Copper (Cu) wires with diameters of $500 \mu\text{m}$ were purchased from Goodfellow. D-Glucose (Glu) 99% from Fisher Scientific was prepared 24 h before use. Phosphate salts (KH_2PO_4 and Na_2HPO_4) and sodium chloride (NaCl) analytical grade were purchased from Acros Organic. The buffered saline pH 7.4 was prepared from phosphate salts (0.1 M) and sodium chloride (0.15 M) is used for the testing of the electrodes.

2.2. Equipment

The set up used for the alternating current (AC) and direct current (DC) treatment of PtCu electrodes was previously described [34]. Briefly, it consisted of an arbitrary waveform generator (5061, Tabor electronics) connected to a bipolar high-voltage operational amplifier (BOP 1000 M, Kepco). The applied waveform was monitored using a digital oscilloscope (Explorer III oscilloscope, Nicolet Instrument Corporation). The outputs of the amplifier are connected to a small electrochemical cell. This electrochemical cell contains two electrodes, a Pt counter electrode and a PtCu electrode which is subjected to AC and DC electric fields in the mixture of polymeric monomer-redox mediator and that is later used as an anode or cathode for FCs as schematically displayed in Fig. 1.

An EG&G 273 potentiostat from Princeton Applied Research was used for the testing of the electrodes. Ag/AgCl was used as a

reference electrode. Voltage and current measurements of the FCs and BFCs were carried out with two multimeters from Fluke 87 True RMS. The FCs and BFCs current and voltage were varied using a potentiometer ($1 \text{ M}\Omega$).

Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray spectroscopy (EDX) were carried out using JEOL JSM 6400. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) was carried out with Model Varian Liberty Series II. Standardization was performed with three Pt and Cu solutions ranging from approximately 1–20 ppm.

2.3. Methodology

A schematic representation on how PtCu is prepared is shown in Fig. 1. Pt wire 3 mm in length and $500 \mu\text{m}$ in diameter was connected to a long Cu wire. A heat-shrink tube was used to insulate the Cu wire by leaving equal surface area of 3 mm Cu uncovered. One of the PtCu electrodes that is later used as cathode or anode for FCs is immersed in small cell with a capacity of 3 mL containing 0.5 mL ultrapure water, $10 \mu\text{L}$ benzene sulfonic acid (BSA) obtained by dissolving 4 mg BSA in 1 mL ultrapure water and, $10 \mu\text{L}$ phenol obtained by dissolving 15 mg phenol in 1 mL ultrapure water. The mixture was left under constant stirring then PtCu electrode was subjected to 30 Hz, $180 \text{ V}_{\text{p-p}}$ AC and 10 V offset DC for 5–10 min. During this treatment BSA, polyphenol (PP) and Pt–Cu issued from corrosion of PtCu substrate under AC and DC positive signals were deposited on the PtCu substrate to form PtCu covered by (BSA-PP-Pt-Cu), abbreviated as PtCu(BSA-PP-Pt-Cu) electrode.

For use in GBFCs, the bioanode is prepared by similar procedure as described above, but by adding 4 mg glucose oxidase into the benzene sulfonic acid–phenol solution to form PtCu covered by (BSA-PP-Pt-Cu-GOx), abbreviated as PtCu(BSA-PP-Pt-Cu-GOx) bioanode. The preparation of the biocathode followed similar process, but by replacing benzene sulfonic acid by $40 \mu\text{L}$ 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) in the presence of 3 mg laccase to form PtCu covered by (ABTS-PP-Pt-Cu-Lac), abbreviated as PtCu(ABTS-PP-Pt-Cu-Lac) biocathode.

3. Results and discussion

3.1. AC and DC treatment of PtCu bi-metal electrode

The deposition and manufacturing of electrodes under electrochemical control is a very attractive process because a range of parameters such as voltage, current, deposition time, frequency can be controlled to yield deposits with desired thicknesses and morphologies [35,36]. Furthermore, this kind of processes can easily be automated thus leading to high reproducibility [35,36]. Fig. 1 depicts the simultaneous use of direct and alternating current electrochemical processes for the automated treatment of PtCu bi-metal electrode for use in FCs and BFCs. First, Pt and Cu wires were connected together to form a bi-metal electrode as illustrated in Fig. 1. Afterward, PtCu electrode was immersed in a mixture of benzene sulfonic acid–phenol or 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid)–phenol which after treatment under AC and DC fields yield an electrode capable of generating energy. It is worth noting that without the simultaneous DC and AC treatment of PtCu under the mentioned conditions, no significant energy was delivered from the untreated PtCu electrodes.

Fig. 2B(2) illustrates SEM image of the treated Pt part of PtCu bi-metal electrode under the conditions mentioned above to form (BSA-PP-Pt-Cu) deposit. The deposit shows a black color and a rough morphology if compared to the untreated Pt part of PtCu substrate depicted in Fig. 2B(1). The thickness of the deposited film estimated using SEM of a cross section of the electrode was

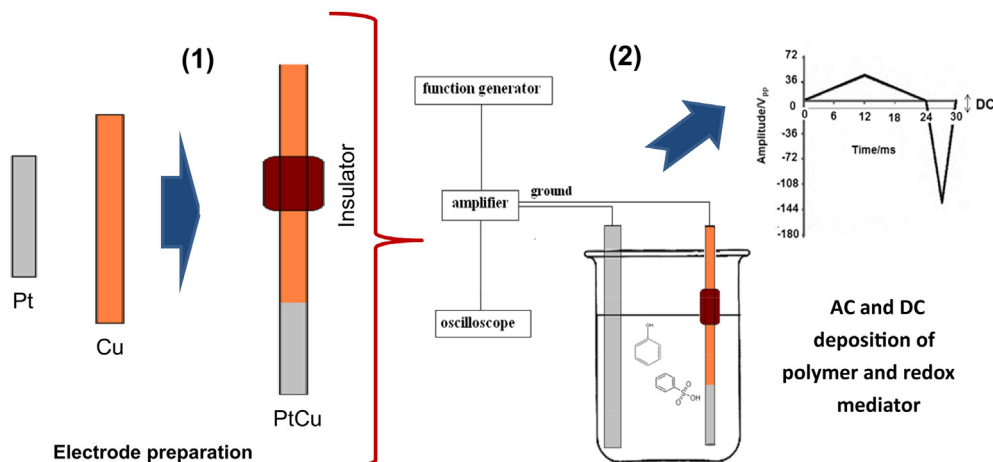


Fig. 1. Schematic representation showing the preparation of PtCu and PtCu(BSA-PP-Pt-Cu) electrodes. Step 1. Connection between Pt and Cu wires to form PtCu substrate. Step 2. AC and DC treatment of PtCu in benzene sulfonic acid - phenol solution to form PtCu(BSA-PP-Pt-Cu).

found to be $\sim 30\text{--}40\text{ }\mu\text{m}$. The analytical details of the elemental composition determined by EDX of the deposited film are gathered in Table 1. It must be pointed out that carbon (C) is the dominant element in the composition of the deposited film. This shows that the deposit is mainly composed of carbon-based polymer which would be polyphenol that is electropolymerized from the phenol monomer present in the solution under 10 V offset DC. The presence of large amount of Cu and Pt in the film is not surprising since during the treatment of PtCu bi-metal with simultaneous AC and DC fields, Cu and Pt will corrode under the DC and AC positive polarizations, especially during the first stages of the treatment when no polymer is yet deposited. Afterwards, the Cu and Pt cations issued from the corrosion will in turn be electrodeposited during the negative polarization of the AC field to yield Pt and Cu entrapped in the deposited polymer membrane. Table 1 also depicts the presence of other elements such as O, S which are related to presence of BSA in the film. The presence of unexpected elements like Na and Cl is ascribed to eventual contaminations from the employed chemicals or from the EDX probe. The EDX analyses confirm the presence of BSA-PP-Pt-Cu in the deposit as suggested previously.

3.2. Polarization curves of the AC and DC treated PtCu substrate

Fig. 3 compares the polarization curves of the deposited films on PtCu substrates treated with DC and AC fields in the solution of

benzene sulfonic acid–phenol to form PtCu(BSA-PP-Pt-Cu) tested as an anode and as a cathode in phosphate buffer solution at neutral pH. It will be noted that the oxidation process at PtCu(BSA-PP-Pt-Cu) begins at -0.30 V vs. Ag/AgCl and the reduction process starts at $+0.25\text{ V}$ vs. Ag/AgCl. Hence, using the same electrode, PtCu(BSA-PP-Pt-Cu), a cell voltage of at least 400 mV can be obtained. These results suggest that a FC can be constructed from the same PtCu(BSA-PP-Pt-Cu) electrodes. The reason for that may have to do with the formation of some kind of micro-batteries in the deposited film that contain Pt, Cu, polyphenol and benzene sulfonic acid on PtCu substrate [33] (further discussions on micro-batteries can be found in Section 3.3). The current densities of PtCu(BSA-PP-Pt-Cu) as an anode and as a cathode are also in the same order of magnitude. Thus, no significant limitation from the oxidation or the reduction reactions will affect the power output of the FC based PtCu(BSA-PP-Pt-Cu) electrodes. The latter is reflected in its stability which is found to be pretty good as it will be discussed later in Section 3.4. On the other hand, Fig. 3 clearly depicts that PtCu unsubjected to AC and DC fields in benzene sulfonic acid–phenol solution yield neither a substantial current nor potential to suggest an eventual generation of power. Finally, it is worth noting that the presence of a redox wave in the oxidation and reduction linear sweep voltammograms of PtCu(BSA-PP-Pt-Cu) (Fig. 3) might be related to presence of an electroactive specie in the deposited film that is probably due to either a Cu redox couple, polyphenol or benzene sulfonic acid that contain an aromatic ring.

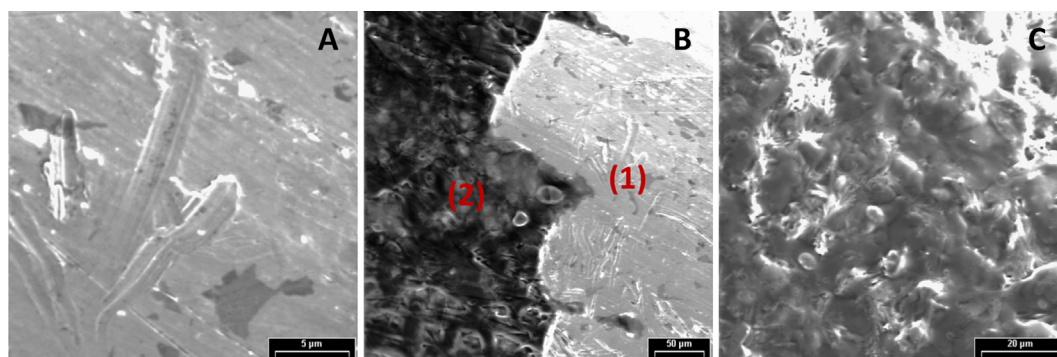


Fig. 2. Scanning electron microscopy images of Pt part in PtCu electrode before treatment (A and B(1)) and, after treatment at 30 Hz, 180 V_{pp} AC and 10 V offset DC for 5–10 min in benzene sulfonic acid–phenol solution to deposit BSA-PP-Pt-Cu (B(2) and C).

Table 1

EDX elemental analysis of the deposited film on PtCu substrate subjected to AC and DC fields in a mixture of benzene sulfonic acid–phenol to form (BSA-PP-Pt-Cu) deposit.

Element	Line	Weight%	K-ratio	Decon regions	Cnts/s	Atomic%
C	Ka	61.23	0.5694	0.110–0.370	1.98	88.28
O	Ka	4.58	0.0425	0.340–0.720	0.44	4.96
Na	Ka	0.56	0.0052	0.800–1.300	7.46	0.42
S	Ka	2.90	0.0269	2.120–2.500	1.64	1.57
Cl	Ka	1.17	0.0158	2.420–2.820	1.90	0.53
Cu	Ka	10.85	0.0823	7.700–8.360	5.40	2.41
Pt	La	20.18	0.1876	9.020–9.780	1.81	1.79
Total		100.00				

3.3. Power density of the AC and DC treated PtCu electrode

In order to verify the results of the polarization curves and the hypothesis of formation of micro-batteries in PtCu(BSA-PP-Pt-Cu), two PtCu(BSA-PP-Pt-Cu) electrodes were placed in small cell with a capacity of 7 mL containing 5 mL buffer solution at neutral pH. The two electrodes were connected to two multimeters, one for potential recording and the other for current reading. The voltage and current are varied using 1 MΩ potentiometer. Fig. 4A displays how the power density ($P_{\text{cell}} = E_{\text{cell}} \times J_{\text{cell}}$) determined by the cell voltage (E_{cell}) and the cell current density (J_{cell}) of the FCs based PtCu(BSA-PP-Pt-Cu) anode and PtCu(BSA-PP-Pt-Cu) cathode varies with cell voltage. One can clearly see that the FC based PtCu(BSA-PP-Pt-Cu) electrode used as anode and cathode reaches a maximum power density of $10.8 \mu\text{W mm}^{-2}$ at a cell voltage of 0.19 V (Fig. 4A). This power density is 150 fold higher than the PtCu segments nano-batteries proposed recently by Liu et al. [33]. The latter would mainly be attributed to the AC and DC treatment of PtCu bi-metal substrate in the benzene sulfonic acid–phenol solution. On the other hand, it is found that when PtCu(BSA-PP-Pt-Cu) electrode is immersed in buffer solution with the Pt and Cu ends connected together, the electrode delivered a maximum power density of $\sim 4.58 \mu\text{W mm}^{-2}$. Thus, one can suggest that the substantial power density produced by the FC based PtCu(BSA-PP-Pt-Cu) anode and PtCu(BSA-PP-Pt-Cu) cathode observed in Fig. 4A

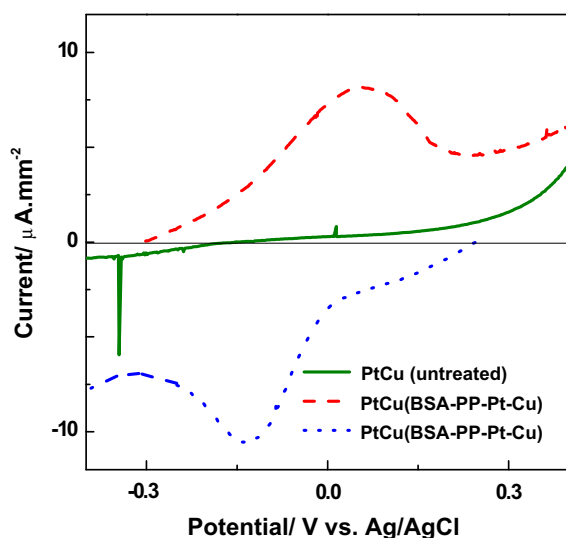


Fig. 3. Polarization curves of PtCu(BSA-PP-Pt-Cu) as a FC anode and cathode. Also is shown the polarization curve of untreated PtCu. Testing conditions: phosphate buffer pH 7.4 (0.1 M KH_2PO_4 + 0.1 M Na_2HPO_4 + 0.15 M NaCl) under air at room temperature.

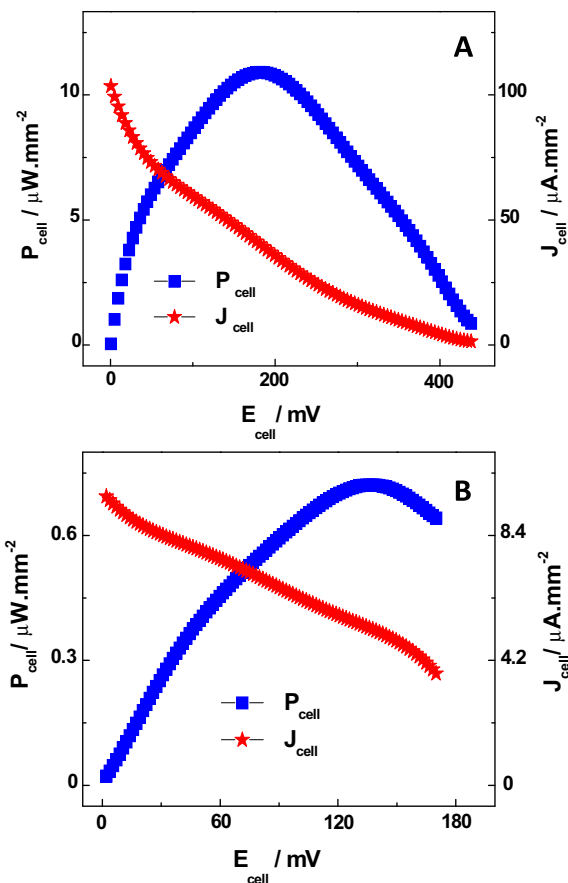


Fig. 4. (A) Current density-cell voltage and power density-cell voltage of the non-compartmentalized FCs based PtCu(BSA-PP-Pt-Cu) as an anode and a cathode. (B) The same as (A), but by replacing phenol by pyrrole to form PtCu(BSA-PPy-Pt-Cu) electrode. Testing conditions: phosphate buffer pH 7.4 (0.1 M KH_2PO_4 + 0.1 M Na_2HPO_4 + 0.15 M NaCl) under air at room temperature.

would actually be delivered by two batteries connected in parallel that doubles the power density as schematically displayed in Fig. 5.

Although at this stage the mechanisms of power generation from PtCu(BSA-PP-Pt-Cu) electrodes are not yet fully clear and require in depth studies, our results suggest that when Pt is connected to a Cu wire and put in buffer solution, the large difference in potential would theoretically generate a power. However, because Pt is directly linked to Cu, most of the generated power is wasted in short circuit (Fig. 3) [33]. Subjecting PtCu bi-metal to 30 Hz, 180 V_{p-p} AC and 10 V offset DC in benzene sulfonic acid–phenol solution would probably corrode some of the Cu and eventually Pt under the positive AC and DC polarizations and simultaneously electrodeposits the dissolved Cu and Pt cations during the negative half period of the AC signal. The presence of phenol monomer in the solution leads to its electropolymerization at 10 V DC to form polyphenol, along with the deposited Cu and Pt as previously evidenced by EDX analysis of the deposit (Table 1). On the other hand, polyphenol as non-conducting polymer would play a bridge for the deposited galvanic couple Pt-Cu that would form some kind of micro-batteries. The evidence to this statement lies in Fig. 4B which shows that replacement of phenol monomer by pyrrole leads to substantial drop in power output of the FC based PtCu(BSA-PPy-Pt-Cu) electrodes. Because electropolymerization of pyrrole at 10 V DC leads to polypyrrole (PPy), a conducting polymer, as a result the deposited Pt and Cu would again be short circuited, leading to loss in power. The presence of BSA in the polyphenol

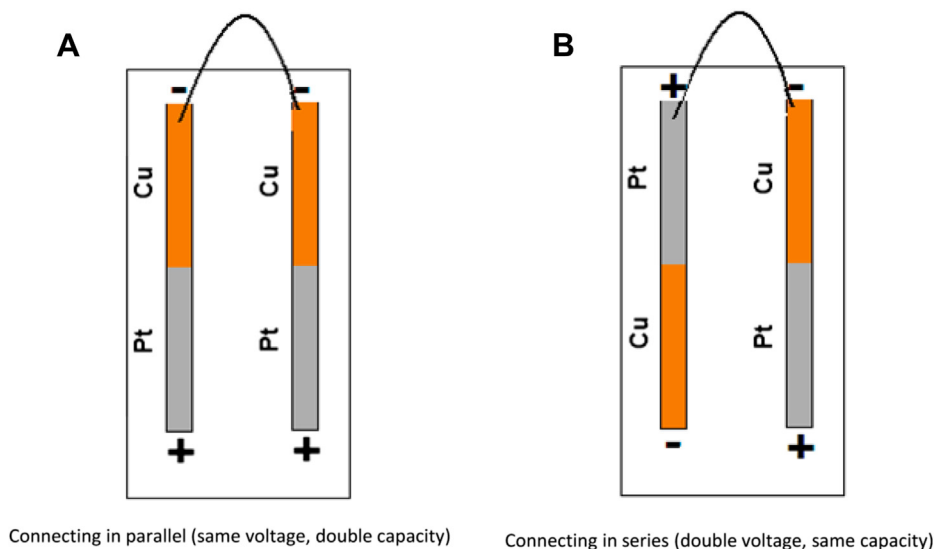
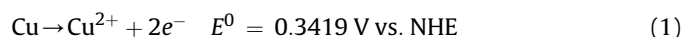
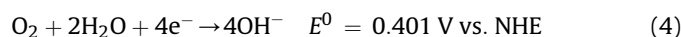
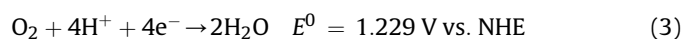
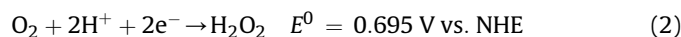


Fig. 5. Schematic representation of two PtCu(BSA-PP-Pt-Cu) electrodes connected in parallel (A) and in series (B) and their electrical characteristics.

matrix would be beneficial to promote a better proton exchange in the polyphenol membrane because of the presence of sulfonic acid groups [37–40]. Under these circumstances, the driven reactions in PtCu(BSA-PP-Pt-Cu) micro-batteries would mainly be the dissolution of the deposited Cu due to presence of NaCl in buffer solution following Eq. (1). This would constitute the cathodic pole of the micro-batteries [41,42]:



In fact, results from the ICP analyses showed the presence of Cu ions traces in the buffer solution where the FCs were tested. The anodic pole of the micro-batteries would be Pt at which O_2 is reduced to either H_2O_2 , H_2O or OH^- following Eqs. (2)–(4) [43]:



3.4. Stability

The stability of the FC based PtCu(BSA-PP-Pt-Cu) electrodes as an anode and a cathode was evaluated in phosphate buffer solution pH 7.4 under air at room temperature for 5 weeks of non-continuous operation and 3 days of continuous working. As displayed in Fig. 6A, the FC retains more than ~94% of its performance in buffer solution when operated continuously for more than 3 days. This is the equivalent to ~2% loss per day. When the FC is tested at regular intervals in the physiological electrolyte, it retains more than ~88% after 5 weeks as depicted in Fig. 6B. The slight losses in power density of the FCs after the continuous or interrupted operations would probably be related to dissolution or corrosion of the deposited Cu as revealed by ICP analysis that showed the presence of Cu ions traces in the testing buffer solution. Another reason for the power losses may have to do with the rearrangement of deposited Pt–Cu sites in the polyphenol membrane that may lead to deactivation of some of the deposited Pt–Cu micro-batteries.

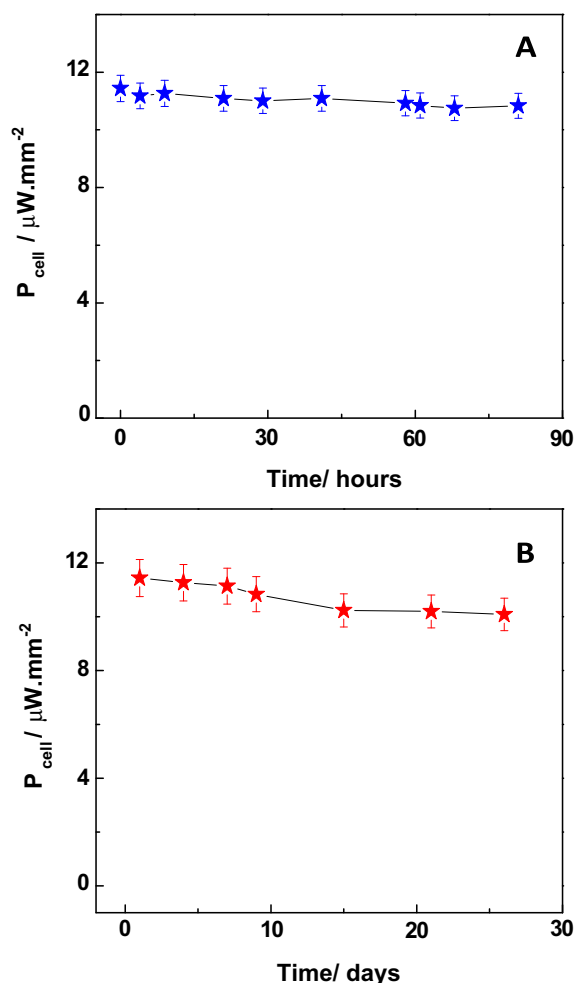
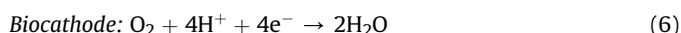


Fig. 6. Stability of the PtCu(BSA-PP-Pt-Cu) based FC for 3–4 days of continuous operation (A) and, 5 weeks of interrupted operation (B). Testing conditions: phosphate buffer (0.1 M KH_2PO_4 + 0.1 M Na_2HPO_4 + 0.15 M NaCl) pH 7.4 under air at room temperature.

4. Application to glucose/O₂ BFCs

The considerable power density as well as the pretty good stability of the FCs constructed from PtCu(BSA-PP-Pt-Cu) electrodes prompted us to test them for glucose/O₂ BFCs. For that, the bioanode was constructed by similar procedure as previously mentioned for PtCu(BSA-PP-Pt-Cu), but by adding glucose oxidase to the solution. The biocathode was prepared by the same procedure, but by adding laccase enzyme to the mixture and replacing BSA by ABTS. ABTS was selected for the biocathode because (i) it has similar sulfonic acid groups as BSA that will promote a better proton exchange in the polyphenol membrane and, (ii) it was found to be a better electron mediator for laccase enzyme. By contrast, BSA was found to be a better redox mediator for GOx. Addition of GOx at the anode to form PtCu(BSA-PP-Pt-Cu-GOx) bioanode leads to further increase in the current density as shown in Fig. 7A. The latter is due to the additional biocatalytic oxidation of glucose by the deposited GOx in the film that delivers further electrons following Eq. (5), thus enhances the oxidation current.



On the other hand, addition of laccase enzyme into PtCu(ABTS-PP-Pt-Cu) cathode to form PtCu(ABTS-PP-Pt-Cu-Lac) biocathode

enhances also the catalytic current due to O₂ reduction by the deposited laccase enzyme because Lac enzyme catalyzes O₂ reduction following Eq. (6) (comparison between the linear sweep voltammograms due to reduction of Fig. 7B vs. Fig. 3).

In order to study accurately the activity of the deposited enzyme, PtCu(BSA-PP-Pt-Cu-GOx) bioanode was further tested using amperometry. Fig. 7C illustrates a comparison of current response to one injection of 5 mM glucose of PtCu(BSA-PP-Pt-Cu-GOx) electrode and 5 mg GOx dissolved in 5 mL buffer solution tested at clean Pt electrode. It will be noted that PtCu(BSA-PP-Pt-Cu-GOx) bioanode responds efficiently to glucose demonstrating that the deposited GOx still active and decomposes efficiently the analyte glucose. Furthermore, the current response of PtCu(BSA-PP-Pt-Cu-GOx) bioanode is quite high with respect to freely dissolved GOx. The latter is understandable because the deposited GOx has higher local concentration due to thickness of the deposit [42]. By contrast, the freely dissolved GOx has its concentration dispersed in 5 mL solution and only the electrons generated from glucose oxidation carried out by the GOx molecules located in the diffuse double layer of the electrode will account [42]. Also, Fig. 7C displays that the current response to glucose using PtCu(BSA-PP-Pt-Cu-GOx) bioanode tends to a plateau, characteristic of a diffusion limited process, while for the freely dissolved enzyme, there is a continuous increase of the current response with time, characteristic of a kinetic control [42].

Fig. 7B shows that in presence of enzymes, the catalytic oxidation of glucose at PtCu(BSA-PP-Pt-Cu-GOx) bioanode begins

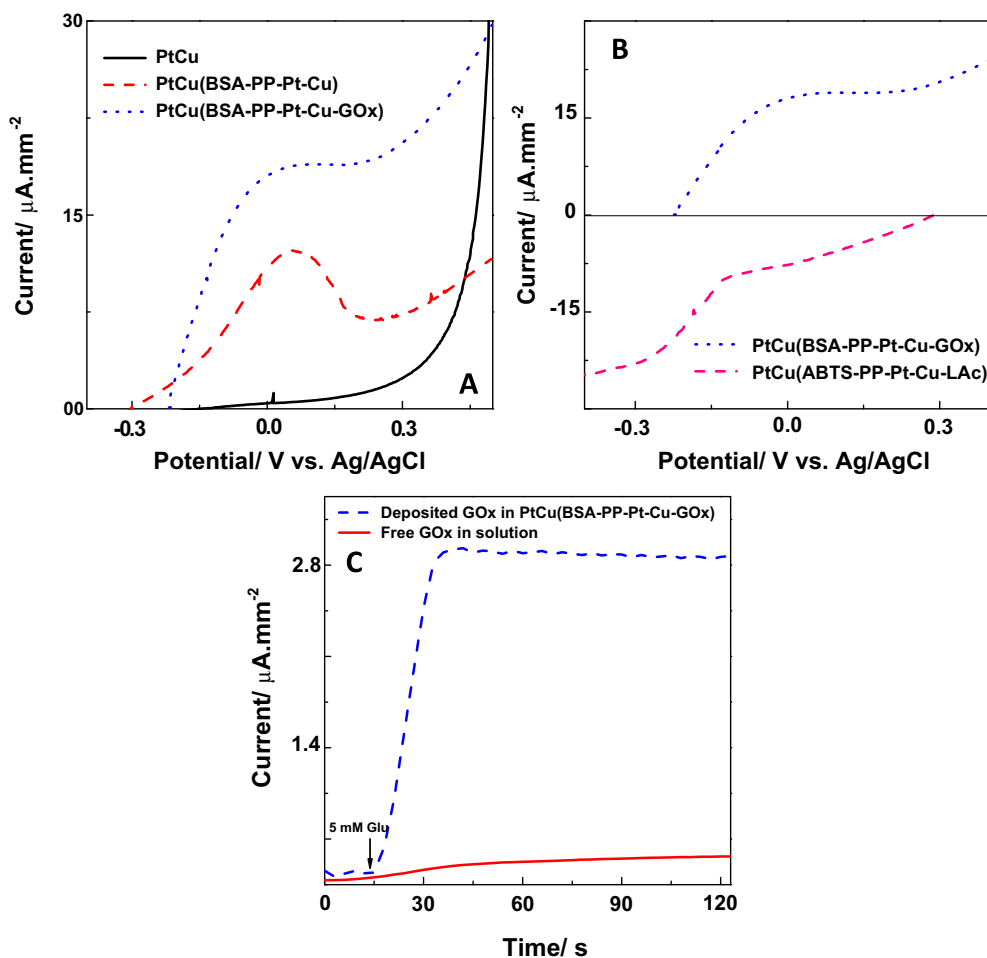


Fig. 7. (A) Comparison between the anodic polarization curves of untreated PtCu substrate, PtCu(BSA-PP-Pt-Cu) and PtCu(BSA-PP-Pt-Cu-GOx) anodes. (B) Polarization curves of the BFC based PtCu(BSA-PP-Pt-Cu-GOx) bioanode and PtCu(ABTS-PP-Pt-Cu-Lac) biocathode. (C) Amperometric response to 5 mM glucose injection of the deposited GOx in PtCu(BSA-PP-Pt-Cu-GOx) bioanode and 5 mg of freely dissolved GOx in 5 mL buffer solution. Testing conditions: phosphate buffer pH 7.4 (0.1 M KH₂PO₄ + 0.1 M Na₂HPO₄ + 0.15 M NaCl) containing 10 mM glucose under air at room temperature. (C) is obtained using constant stirring of the testing buffer solution.

Table 2

Characteristics of the BFC based PtCu(BSA-PP-Pt-Cu-GOx) bioanode and PtCu(ABTS-PP-Pt-Cu-LAs) biocathode.

Electrode surface area PtCu	9.81 mm ²
Electrolyte	Buffer pH 7.4 with 10 mM glucose
Operating potential/V	0.56 ± 0.02
Maximum power density/ μ W	130.51 ± 7.50
[$P_{\text{cell}}(\text{day } 35)/P_{\text{cell}}(\text{day } 1)]/100/\mu\text{W}$ (non-continuous operation)	84 ± 6%
Continuous operation [$P_{\text{cell}}(\text{day } 3)/P_{\text{cell}}(\text{day } 1)]/100/\mu\text{W}$	91 ± 4%

at ~ -0.22 V vs. Ag/AgCl and reaches a maximum current of $\sim 22.72 \mu\text{A mm}^{-2}$ at $+0.4$ V. The electrocatalytic reduction of O_2 at PtCu(ABTS-PP-Pt-Cu-LAc) biocathode appears at $+0.27$ V vs. Ag/AgCl and attains a maximum current of $\sim -24.95 \mu\text{A mm}^{-2}$ at -0.4 V. Thus, no limitation from the bioanode or biocathode that may affect its stability can be noticed. Table 2 gathers the characteristics of the manufactured GBFC based PtCu(BSA-PP-Pt-Cu-GOx) bioanode and PtCu(ABTS-PP-Pt-Cu-LAc) biocathode in phosphate buffer solution pH 7.4 containing 10 mM glucose. It can be seen that the GBFC reaches a maximum power density of $\sim 13.3 \mu\text{W mm}^{-2}$ at cell voltage of 0.56 V. However, it is important to remind that 76% of the power is produced by the PtCu bi-metal electrodes subjected to AC and DC fields and, only the remaining 24% is delivered by the enzyme reactions. This power density challenges most of the enzyme based GBFCs reported to date [10,12,17–24]. The latter is essentially due to PtCu material prepared under the described conditions, which boost the power output of the GBFC. On the other hand, it is worth noting that no significant difference in the delivered energy is noticed when BSA is replaced by ABTS. Consequently, the power output of the FC based on PtCu(BSA-PP-Pt-Cu) anode and PtCu(ABTS-PP-Pt-Cu) cathode was estimated to $\sim 10.1 \mu\text{W mm}^{-2}$. Thus, the increase in power density of the GBFC with respect to PtCu(BSA-PP-Pt-Cu) would mainly be attributed to presence of enzymes in the deposited films. Table 2 also displays that the GBFC retains more than $\sim 91\%$ of its performance in buffer solution when operated continuously for more than 3 days. This is the equivalent of $\sim 3\%$ loss per day, a value better than previously reported performances [10,15–24]. When the GBFC is tested at regular intervals in the physiological electrolyte, it retains more than $\sim 85\%$ after 5 weeks. Comparison of the stability values between the GBFC and FC (Table 2 vs. Fig. 6) indicate that the BFC is less stable than the FC. This make sense because the fragile part in the electrode is the biochemical material based enzymes GOx and LAc that may undergo a quick deterioration compared to the FC material.

5. Conclusions

In summary, we demonstrated how bi-metal PtCu connected wires immersed in a solution of benzene sulfonic acid (BSA)–phenol (P) or 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS)–phenol (P), then subjected to simultaneous alternating current (AC) and direct current (DC) electric fields generate power. We showed that PtCu covered by the deposited film that contain (BSA-PP-Pt-Cu), abbreviated as PtCu(BSA-PP-Pt-Cu) electrode, plays the role of a substantial anode and cathode. The latter was related to formation of micro-batteries in the deposited film (BSA-PP-Pt-Cu) that are able to take or deliver electrons from the deposited Pt and Cu, respectively. PP-BSA may play the role of bridge for proton conduction in the formed micro-batteries. The power density of the fuel cell (FC) based PtCu(BSA-PP-Pt-Cu) anode and PtCu(BSA-PP-Pt-Cu) cathode in phosphate buffer solution pH 7.4 at room temperature reaches $\sim 10.8 \mu\text{W mm}^{-2}$. Addition of enzymes, glucose oxidase

at the anode and laccase at the cathode and, replacement of BSA by ABTS at the cathode in the deposited films on PtCu substrates increases the power density to $13.3 \mu\text{W mm}^{-2}$. The latter is related to enzyme reactions that oxidize glucose at the bioanode using glucose oxidase, hence generating further electrons with which O_2 is further reduced at the biocathode by the deposited laccase enzyme. Also, it is shown that the FCs and glucose biofuel cells (GBFCs) have a pretty good stability when operated continuously or interruptedly. This new process might be of great relevance for the construction of a new generation of FCs that operate at mild conditions or to boost the power outputs of BFCs and make them suitable for diverse applications. Based on these findings, one can imagine the substantial energy or voltage which can be delivered if a large number of these micro-electrodes are connected in parallel or in series and, from environmentally friendly physiological electrolytes.

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References

- [1] A.B. Stambouli, E. Traversa, Renewable and Sustainable Energy Reviews 6 (2002) 295.
- [2] K. Kordesch, G. Simader, Fuel Cells and Their Applications, VCH, Weinheim, 1996.
- [3] C. Lamy, S. Rousseau, E.M. Belgsir, C. Coutanceau, J.M. Léger, Electrochimica Acta 49 (2004) 3901.
- [4] S. Wasmus, A. Küver, Journal of Electroanalytical Chemistry 461 (1999) 14.
- [5] A. Bazylak, International Journal of Hydrogen Energy 34 (2009) 3845.
- [6] S. Zhang, X.Z. Yuan, J.N.C. Hin, H. Wang, K.A. Friedrich, M. Schulze, Journal of Power Sources 194 (2009) 588.
- [7] L. Carrette, K.A. Friedrich, U. Stimming, ChemPhysChem 1 (2000) 162.
- [8] M.J. Cooney, V. Svoboda, C. Lau, G. Martina, S.D. Minter, Energy & Environmental Science 1 (2008) 320.
- [9] T. Miyake, S. Yoshino, T. Yamada, K. Hata, M. Nishizawa, Journal of the American Chemical Society 133 (2011) 5129.
- [10] M. Ammam, J. Fransaer, Biotechnology and Bioengineering 109 (2012) 1601.
- [11] S.D. Minter, B.Y. Liaw, M.J. Cooney, Current Opinion in Biotechnology 18 (2007) 228.
- [12] J. Kim, H. Jia, P. Wang, Biotechnology Advances 24 (2006) 296.
- [13] S.C. Barton, J. Gallaway, P. Atanassov, Chemical Reviews 104 (2004) 4867.
- [14] A. Heller, Physical Chemistry Chemical Physics 6 (2004) 209.
- [15] X. Zhao, H. Jia, K. Kim, P. Wang, Biotechnology and Bioengineering 104 (2009) 1068.
- [16] P. Cinquin, C. Gondan, F. Giroud, S. Mazabrard, A. Pellissier, F. Boucher, J. Alcazar, P.K. Gorgy, F. Lenouvel, S. Mathe, P. Porcu, S. Cosnier, PloS One 5 (2010) e10476.
- [17] F. Gao, Y. Yan, L. Su, L. Wang, L. Mao, Electrochemistry Communications 9 (2007) 989.
- [18] C.M. Yu, M.J. Yen, L.C. Chen, Biosensors and Bioelectronics 25 (2010) 515.
- [19] J. Ryu, H.S. Kim, H.T. Hahn, D. Lashmore, Biosensors and Bioelectronics 25 (2010) 1603.
- [20] M. Zhou, L. Deng, D. Wen, L. Shang, L. Jin, S. Dong, Biosensors and Bioelectronics 24 (2009) 2904.
- [21] J. Naruse, L.Q. Hoa, Y. Sugano, T. Ikeuchi, H. Yoshikawa, M. Saito, E. Tamiya, Biosensors and Bioelectronics 30 (2011) 204.
- [22] Y. Yan, W. Zheng, L. Su, L. Mao, Advanced Materials 18 (2006) 2639.
- [23] L. Brunel, J. Denel, K. Servat, K.B. Kokoh, C. Jolival, C. Innocent, M. Cretin, M. Rolland, S. Tingry, Electrochemistry Communications 9 (2007) 331.
- [24] M. Ammam, J. Fransaer, Biosensors and Bioelectronics 25 (2010) 1474.
- [25] R. Srivastava, P. Mani, N. Hahn, P. Strasser, Angewandte Chemie International Edition 46 (2007) 8988.
- [26] S. Koh, N. Halm, P. Strasser, ECS Transactions 3 (2006) 139.
- [27] M. Oezaslan, F. Hasche, P. Strasser, Journal of the Electrochemical Society 159 (2010) B444.
- [28] K. Jayasayee, J.A. Rob Van Veen, T.G. Manivasagam, S. Celebi, E.J.M. Hensen, F.A. de Bruijn, Applied Catalysis B: Environmental 111–112 (2012) 515.
- [29] M. Oezaslan, P. Strasser, Journal of Power Sources 196 (2011) 5240.
- [30] T. Page, R. Johnson, J. Hormes, S. Noding, B. Rambabu, Journal of Electroanalytical Chemistry 485 (2000) 34.
- [31] H. Yanga, L. Daia, D. Xub, J. Fangb, S. Zou, Electrochimica Acta 55 (2010) 8000.
- [32] D. Xu, Z. Liu, H. Yang, Q. Liu, J. Zhang, J. Fang, S. Zou, K. Sun, Angewandte Chemie International Edition 48 (2009) 4217.

- [33] R. Liu, A. Sen, *Journal of the American Chemical Society* 133 (2011) 20064.
- [34] M. Ammam, J. Fransaer, *Biosensors and Bioelectronics* 25 (2009) 191.
- [35] L. Besra, M. Liu, *Progress in Materials Science* 52 (2007) 1.
- [36] M. Ammam, *RSC Advances* 2 (2012) 7633.
- [37] P. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, K. Wang, S. Kaliaguine, *Journal of Membrane Science* 229 (2004) 95.
- [38] B. Liu, G.P. Robertson, D.S. Kim, M.D. Guiver, W. Hu, Z. Jiang, *Macromolecules* 40 (2007) 1934.
- [39] J.W. Rhima, H.B. Park, C.S. Lee, J.H. Jun, D.S. Kimb, Y.M. Lee, *Journal of Membrane Science* 238 (2004) 143.
- [40] G. Inzelt, M. Pineri, J.W. Schultze, M.A. Vorotyntsev, *Electrochimica Acta* 45 (2000) 2403.
- [41] D. Starosvetsky, O. Khaselev, M. Auinat, Y. Ein-Eli, *Electrochimica Acta* 51 (2006) 5660.
- [42] A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, second ed., Wiley, NY, 2001.